Joint superexchange–Jahn-Teller mechanism for A-type antiferromagnetism in $LaMnO_3$

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We propose a mechanism for A-type antiferromagnetism in orthorombic $LaMnO_3$, compatible with the large Jahn-Teller splitting inferred from structural data. Orbital ordering resulting from Jahn-Teller distortions effectively leads to A-type ordering (antiferromagnetic in the c axis and ferromagnetic in the ab plane) provided the in-plane distorsion Q_2 is large enough, a condition generally fulfilled in existing data.

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Stoichiometric $LaMnO_3$ (LMO) is known [1] to be an A-type antiferromagnetic insulator (A-AFMI), where ferromagnetically ordered MnO_2 planes (in the xy direction) have staggered magnetization along the z axis. Upon increasing the temperature a paramagnetic insulating phase (PMI) is reached. On the other hand sufficient hole doping (e.g. by substituting La with Sr or Ca) gives rise via the so-called double-exchange hopping mechanism [2,3] to a low-temperature ferromagnetic metallic phase (FMM) turning into a PMI phase at higher temperature. Not only magnetism determines the main physical properties, in fact both theoretical [4,5] and experimental [6] evidences emphasize the relevance of electron-lattice coupling. Charge and orbital ordering also occur, further showing the competition between various physical mechanisms. Notice that the crucial role of spin and lattice coupling was repeatedly emphasized to account for the properties of the FMM phase and the FMM-PMI transition at finite doping, as well as charge-ordering phenomena. However, this *liaison* regarded the double-exchange mechanism for charge tranport, being dynamically dressed by lattice degrees of freedom [4–6]. No emphasis was put on the role of static cooperative Jahn-Teller (JT) deformations in stabilizing specific magnetic structures in the AFMI phase.

Here we investigate an approach to the stoichiometric phase of LMO showing that the layered antiferromagnetic structure may result from the interplay between superexchange and JT couplings. Our analysis is alternative to the more qualitative one based on the semicovalent exchange mechanism [7] and is complementary to the superexchange mechanism investigated by Kugel and Khomskii (KK) [8] for perovskites with JT ions. This latter analysis (see also [9]) focused on the interplay between magnetic and orbital ordering within the two e_g orbital manifold, assumed degenerate. In particular, basic ingredients were a strong local electron-electron repulsion U, the Hund coupling J_H between electrons on the two e_g orbitals, and the orbital mixing (described by a mixing angle θ) due to JT distorsion. In the approach of Ref. [8], only e_g (spin and orbital) degrees of freedom were considered, and the spin and orbital order were self-consistently determined to lowest order in J_H/U. The e_g level degeneracy was lifted by superexchange but the JT splitting resulting from the lattice distorsions induced by orbital ordering was not explicitly considered, Only a correction due to a small local JT anharmonicity was introduced. This point of view, considering magnetic exchange to be the main cause of orbital mixing/ordering, but neglecting the orbital splitting resulting from JT effect, might be questioned in LMO where strong JT distorsions arise. Moreover, magnetic exchange interactions are somewhat modest, e.g. $J_{AF} \approx 0.58$ meV and $J_F \approx 0.83$ meV $> J_{AF}$ from inelastic neutron scattering experiments [10], while the KK theory results in $J_F \approx (J_H/U)J_{AF}$, that is J_F much smaller than J_{AF}. Moreover, as pointed out by KK, the observed orthorhombic distorsion with $c < a$ is not expected from considering solely orbital ordering. Therefore, it is not obvious, considering the actual distorsion, that the magnetic A-phase is still the most stable.

According to the experimental evidences for the relevance of the t_{2g} (spin) degrees of freedom, e.g. in the double exchange hopping processes, and for a strong JT coupling, we propose to reconsider the problem. We take properly into account the Hund coupling between e_g and t_{2g} electrons, and assume, contrarily to KK, that the JT splitting is much larger than the exchange energy. This makes the JT effect the driving mechanism for orbital ordering, which in turn controls the magnetic interactions. Hereafter we *assume* some staggered orbital order (i.e. we fix θ on the two sublattices) as determined by strong JT distorsions, without attempting to calculate them, since they can be extracted from crystallographic data. Given the orbital order and the related (relatively large) e_g orbital splitting ϵ, we calculate at any order in ϵ and J_H/U the superexchange interactions. Finally, we determine the parameter ranges which are compatible with the observed A-type AF phase.

For the sake of simplicity we disregard the oxygen sites in the perovskite structure, thus focusing on a single-site model. On each site two Manganese orbitals, the $d_{x^2-y^2}$ (x) and the $d_{3z^2-r^2}$ (z), are available. The real lattice structure is effectively taken into account via the sign and the magnitude of the intersite hopping along the

$x-y-z$ directions. Specifically, we notice that, for a standard choice of phases, the hopping between the d_x and the d_z orbitals on Mn are given by

$$\begin{aligned} t_{xx} = 3t; \quad t_{xz} &= -\sqrt{3}t \text{ along } \hat{\mathbf{x}} \\ t_{zz} = -t; \quad t_{xz} &= \sqrt{3}t, \text{ along } \hat{\mathbf{y}} \\ t'_{zz} = -4t \quad t'_{xx} &= t'_{xz} = 0 \quad . \end{aligned} \tag{1}$$

Throughout this paper the apex indicates hoppings in the z direction. The (static) JT distortions [11] mix the x and z orbitals [5] into a (lower) and b (upper) orbitals with e_g symmetry split by an energy $\epsilon \equiv 2g\sqrt{Q_1^2+Q_2^2}$ where g is an electron-lattice coupling constant. Specifically, using the same notations of Ref. [5] the uniform distortion Q_1 (corresponding to a uniform variation of the lattice parameter along the z direction) couples to the $x-z$ density difference $n_x - n_z$. In systems like LMO, where the lattice spacing in the z direction is shorter that the (average) spacing in the xy plane, the d_z orbitals overlap more and are pushed at higher energy by the Coulomb interaction. Then Q_1 is negative. As pointed out by KK, this disfavours hopping in the z-direction, thus making the JT effect *compete* with the A-type superexchange which alone would imply the opposite distortion. The reverse is true in systems like $KCuF_3$, where the lattice parameter along z is larger than in the xy plane and Q_1 is positive. On the other hand, the distortion Q_2 (opposite on the two sublattices of the xy-planes) corresponds to an alternate contraction and dilation of the Mn-O bonds on the xy plane and mixes the x and z components of the a, b orbitals

$$\begin{aligned} |a\rangle &= \cos(\theta/2)|x\rangle \pm \sin(\theta/2)|z\rangle \\ |b\rangle &= \sin(\theta/2)|x\rangle \mp \cos(\theta/2)|z\rangle \end{aligned} \tag{2}$$

where $\tan(\theta) = Q_2/Q_1$ and the upper (lower) sign is for sites on sublattice 1 (2) of the xy-planes. Accordingly the hoppings between the a and b orbitals of neighbouring sites can straightforwardly be obtained via Eqs. (1).

$$t_{aa} = -t\,(1+2\cos\theta)\,; \tag{3}$$

$$t_{ab} = -t\left(\pm\sqrt{3}+2\sin\theta\right); \quad t_{ba} = -t\left(\mp\sqrt{3}+2\sin\theta\right); \tag{4}$$

$$t'_{aa} = 2t\,(1-\cos\theta)\,; \quad t'_{ab} = t'_{ba} = -2t\sin\theta \tag{5}$$

the upper (lower) sign is for planar hopping in the x (y) direction.

As customarily done, we assume that the Hund coupling between $\sigma = 1/2$ e_g electrons and the $S = 3/2$ spin of the t_{2g} electrons is so large that the initial and final states always have maximal total spin $S_T = 2$. Moreover, and most importantly, we also consider a large local repulsion ($\sim U$) between electrons on Mn sites forbidding to two electrons to reside on the two e_g levels of the same site. Then we work on a reduced Hilbert space with only Mn^{3+} initial and final states [13]

We then carry out a perturbative calculation of both FM and AFM magnetic couplings between sites 1 and 2 by considering second order hopping processes from and to the ground state configuration with one electron per Mn site occupying the lower a orbital. We thus neglect the exchange-induced mixing of e_g orbitals, considered by KK. Notice that this last assumption relies on the JT splitting ϵ being substantially larger than both the temperature and the superexchange scale $\sim t^2/U$. Due to the condition $S_T = 2$, each site $i = 1, 2$ is five times degenerate, $|2, m\rangle_i$ with $m = -2, -1, ..., 2$. The first step consists in forming two-site states with given total spin $J = 0, ..., 4$ from the 25 basis states $|2, m\rangle_1 \otimes |2, m\rangle_2$. The suitable Clebsch-Gordan coefficient are easily obtained. Within each J subspace (the hopping processes conserve the total spin), the hopping perturbation

$$H_t = -\sum_{\sigma;\alpha,\alpha'=a,b} t_{\alpha\alpha'}\left(c^\dagger_{1\sigma\alpha}c_{2\sigma\alpha} + c^\dagger_{2\sigma\alpha}c_{1\sigma\alpha}\right)$$

is applied twice to obtain the $\langle J, M|H_t^2|J, M\rangle$ matrix elements. The double-hopping processes are of two types: aa and ab depending on whether the initial a electron hops on the neighboring a or b orbitals. Accordingly there are two superexchange channels, leading to couplings constants J_{aa} and J_{ab}. The easiest to be calculated is J_{aa} since the Pauli principle forces the two initial a electrons to have opposite spins. As a consequence only one intermediate virtual state per J channel is allowed, with one empty and one doubly occupied a orbital. Both the empty and the doubly occupied orbitals cost an energy $3J'_H/4$, where J'_H is the Hund coupling between e_g and t_{2g} orbitals (the Hund energy is set to zero in the Mn^{3+} ground state configuration). The doubly occupied a orbital has an additional energy cost U. All the intermediate states have then an energy $E_V = U + (3/2)J'_H$ above the ground state energy $E_0 = 0$. As it is standard, the perturbative energy gain can be compared with the energies of $|J, M\rangle$ states as given by the effective Heisenberg model for the aa channel

$$H_{aa} = J_{aa}\left(\mathbf{S}_1 \cdot \mathbf{S}_2 + C\right)$$

with C being a constant energy shift to be determined. The direct comparison provides, besides $C = -4$,

$$J_{aa} = \frac{1}{4}\frac{t_{aa}^2}{U + (3/2)J'_H} \tag{6}$$

This is an effective AFM coupling between electrons on the xy-plane. A similar expression is obtained for the interplane coupling (i.e., in the z direction) J'_{aa}, provided t_{aa} is replaced by t'_{aa} in Eq. (5).

The calculation for J_{ab} is slightly more complicated, since the hopping electron can now give rise on the doubly occupied site to both a $S_T = 5/2$ or a $S_T = 3/2$

state, thus increasing the number of virtual states. However, the same procedure illustrated above yields

$$J_{ab} = -\frac{\overline{t_{ab}^2}}{40}\left(\frac{8}{U'+\epsilon-J_H/2} - \frac{3}{U'+\epsilon-J_H/2+5J'_H/2} - \frac{5}{U'+\epsilon+J_H/2+3J'_H/2}\right) \tag{7}$$

where U' is the local Coulomb repulsion between electrons on the a and b orbitals and

$$\overline{t_{ab}^2} \equiv \frac{(t_{ab}^2+t_{ba}^2)}{2} = t^2\left(3+4\sin^2(\theta)\right). \tag{8}$$

Again the analogous coupling in the z direction can be obtained by replacing t_{ab} and t_{ba} with the corresponding primed quantities of Eq. (5). It can easily be seen that this coupling is ferromagnetic and vanishes when J_H and J'_H are both zero. Notice also that, since J_{ab} arises from virtual hopping $i \to j \to i$ and $j \to i \to j$ and since the a and b orbital combinations are reversed on neighboring sites, the $\overline{t_{ab}^2}$ combination appears, which is the same in the x and y directions [cf. instead (4)]. Thus for each crystalline direction one can write the effective Heisenberg couplings $J = J_{aa} + J_{ab}$ and $J' = J'_{aa} + J'_{ab}$ in the xy planes and z direction respectively. Then the question arises concerning the parameter ranges such that the observed A-type AF is realized. In this case the coupling must be dominantly ferromagnetic in the xy planes and dominantly AF in the z direction. To this purpose we rewrite the J's in the following more compact way

$$J_{aa} = t_{aa}^2/D_{aa}, \quad J_{ab} = -\overline{t_{ab}^2}/D_{ab} \tag{9}$$

The condition that the xy planes are ferromagnetically coupled is written as $|J_{ab}| > J_{aa}$, i.e.

$$\alpha^2 \equiv \frac{\overline{t_{ab}^2}}{t_{aa}^2} > D. \tag{10}$$

where $D = \frac{D_{ab}}{D_{aa}}$. At the same time, the condition for AF coupling in the z direction is expressed by $|J'_{ab}| < J'_{aa}$, that is

$$\alpha'^2 \equiv \frac{{t'_{ab}}^2}{{t'_{aa}}^2} < D. \tag{11}$$

Now, both α and α' (i.e. t_{aa}, $\overline{t}_{ab}$, t'_{aa}, and t'_{ab}) are funtions of θ, or of the JT ratio Q_2/Q_1. Plotting α^2 and α'^2 as a function of $Q_2/|Q_1|$ for $Q_1 < 0$ (the relevant case for LMO), one obtains the curves in Fig. 1. Since from the inequalities (10) and (11), one can deduce the condition

$$\alpha^2 > D > \alpha'^2, \tag{12}$$

the value of D should be below the solid curve and above the dashed ones. The assumed orbital order becomes compatible with A-AFMI order for $Q_2/|Q_1| \gtrsim 2.6$, where the relation (12) can be satisfied. Notice instead that for $Q_1 > 0$ the curve α'^2 is always smaller than α^2, so that no restriction on the Q_2/Q_1 ratio is needed to fulfill the condition (12). This is in agreement with the cooperation between superexchange and JT effect, found in this case, see for example the case of $KCuF_3$ [8].

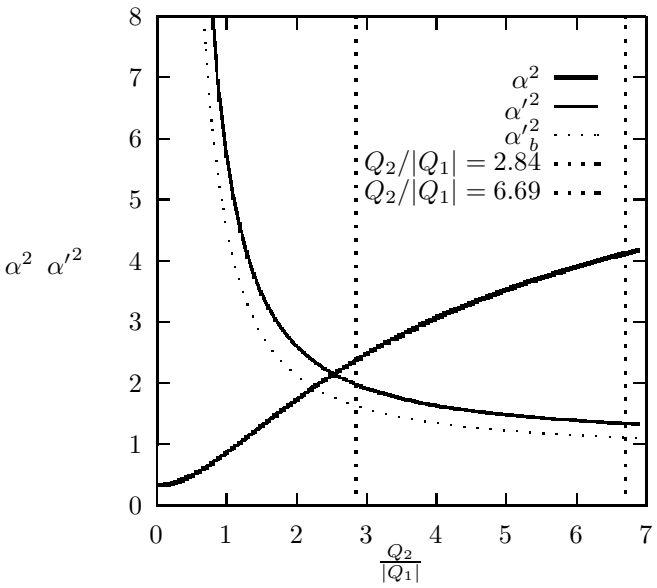

Fig. 1.: α^2 (solid line) and α'^2 (dashed line) as a function of the JT ratio $Q_2/|Q_1|$ for negative Q_1. The dotted line represents α'^2 with $t'_{xz} = 0.05t$. The vertical lines indicate the experimental values $Q_2/|Q_1| = 2.84, 6.69$ (see text)

More precisely we find that

$$\frac{J}{J'} = \frac{t_{aa}^2}{{t'_{aa}}^2}\frac{D-\alpha^2}{D-\alpha'^2} \tag{13}$$

Notice that a substantial amount of $Q_2/|Q_1|$ JT distortion is needed to leave the possility open for the condition (12) to be fulfilled. Using standard results [12] connecting the structural parameters with the $Q_2/|Q_1|$ ratio ($Q_2/|Q_3|$ in the notation of Ref. [12]) we estimated $Q_2/|Q_1| \approx 1.97$ and 6.69 for the parameters of the orthorhombic structures reported in Table V of Ref. [14], while a value 2.84 is obtained from the data related to the crystal where the abovementioned values of J_{AF} and J_F have been measured [10]. Although not all values are compatible with the condition $Q_2/|Q_1| \gtrsim 2.6$, the large variability of the resulting estimates for $Q_2/|Q_1|$ indicates that this parameter may vary from a crystal to another so that the condition $Q_2/|Q_1| \gtrsim 2.6$ is quite reasonable. Especially, we now show that the last one yields values consistent with the observed $J's$.

Let us determine the (hopefully realistic) values of U, U', J_H, J'_H and ϵ providing a D ratio in the needed

range (12). To this purpose we consider typical values of $U = 10$ eV, $U' = U - 2J_H = 6 - 10$ eV, and $\epsilon = 0.1 - 0.5$ eV, and we obtain the ratio D as a function of J_H/U. For simplicity the ratio J_H/J'_H is taken equal to 1. Then, from Fig. 1, we consider typical ranges for D between, e.g., $\alpha'^2 \approx 1.4$ and $\alpha^2 \approx 4.$, roughly corresponding to $Q_2/|Q_1| \approx 6.69$, and $\alpha'^2 \approx 2.$ and $\alpha^2 \approx 2.4$, roughly corresponding to $Q_2/|Q_1| \approx 2.84$. Then we look for what range of J_H/U the conditions $4 > D > 1.4$ or $2.4 > D > 2.$ are realized. In the first case the quite reasonable range $0.1 \lesssim J_H/U \lesssim 0.35$ is found, while in the second case $0.1 \lesssim J_H/U \lesssim 0.15$. The observed values [10] $J = 0.83$ meV (ferro) and $J' = 0.58$ meV (antiferro) are obtained with $J_H = J'_H = 1.25$ eV and $t = 0.34$eV in the case of $Q_2/|Q_1| = 2.84$. This value of t is fairly large, but it can be substantially decreased by taking larger values of $Q_2/|Q_1|$. Notice that, contrarily to the calculations of KK, the planar ferromagnetic coupling can easily be larger than the z-axis antiferromagnetic one. This comes from the ratio $t_{aa}^2/{t'_{aa}}^2$ in (13) where, due to the orbital order stabilized by the JT distortion, hopping in the plane directions is enhanced with respect to the z-axis.

In conclusion, we have illustrated the possibility of an alternative mechanism for the layered antiferromagnetism of the stoichimetric LMO compound. In particular, we showed that the superexchange mechanism, together with strong JT planar distortions, can be responsible for the specific A-type magnetic structure. Like in the analysis of Ref. [8], the sinergetic effect of both magnetic superexchange and orbital ordering is a crucial ingredient. However, contrary to the assumption of Ref. [8], in the present scenario, we assumed a given orbital ordering strongly lifting the degeneracy of the e_g orbitals ($\epsilon \gg J_{ab}, J_{aa}$). A relevant role here is also played by the t_{2g} spin degrees of freedom, as seen from the expressions (6) and (7), which depend rather strongly on J'_H.

Despite the basic differences between our scheme and the proposal of Ref. [8], we find some similarities in the overall result. Specifically we find that for systems with positive Q_1, like, e.g., $KCuF_3$, no restriction is needed on the Q_2/Q_1 ratio to make the orbital ordering compatible with A-AFMI magnetic structure. This is not the case for negative Q_1, where the above discussed conditions have to be imposed on $Q_1/|Q_2|$ and, consequently on the values of J_H/U. Similar values of the J_H/U were found in [8].

Within the present model, to be more realistic one should also take into account the existence of tilt distortions and consider the effects of non vanishing transfer integrals t'_{xx} and t'_{xz}. In fact these hopping constants are strictly zero only for lattices without tilting of the MnO_6 octaedra around axes on the xy plane. We have found that positive t'_{xz} and negative t'_{xx} favour A-type ordering. Another contribution to the problem is the antiferromagnetic exchange originating from t_{2g} electrons. Finally, a full calculation involving all superexchange processes should be feasible.

We stress again that the mechanism proposed here is based on the tight interplay of lattice and electronic degrees of freedom existing even in the undoped LMO system, and that it is aimed to correlate the magnetic ordering with the JT distortions. Justifying the values of Q_1 and Q_2 from microscopic grounds is beyond the scope of the present paper. Some mixing between lattice and spin dynamics and isotopic or pressure dependence of the spin-wave velocity are expected to be rather natural consequences of the proposed scenario.

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